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LETTER TO THE EDITOR

Brillouin scattering investigation of the high temperature diffuse phase transition in Li_2S

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Abstract. The set of acoustic mode frequencies associated with elastic constants C_{11} , C_{12} and C_{44} have been determined from high temperature Brillouin scattering measurements on the anti-fluorite structured compound Li_2S . These decrease linearly from 300 to 800 K, but above 800 K substantial reductions occur in C_{11} and C_{12} . The results are interpreted in terms of normal thermal expansion and a diffuse superionic transition involving Frenkel disorder on the lithium sublattice.

The high temperature diffuse phase transition which results in superionic conductivity in the halide fluorites has been studied by a large number of techniques (Chadwick 1983). Brillouin scattering methods provide a characteristic signature for this transition: certain acoustic mode frequencies and the associated elastic constants reduce significantly above a transition temperature T_c associated with the onset of disorder (Catlow *et al* 1978, Comins *et al* 1990).

Evidence for similar transitions is being sought in anti-fluorite compounds: recent work in this regard includes that by Farley *et al* (1988), Hull *et al* (1988) and Strange *et al* (1990) on Li_2O , and by Hutchings *et al* (1988) on Mg_2Si . A class of anti-fluorite compounds of considerable interest are the alkali sulphides. In particular the neutron scattering work by Buehrer *et al* (1991) on polycrystalline Li_2S provides evidence for substantial thermally-induced disorder on the lithium sublattice at temperatures near 900 K. The results were consistent with the population of cube-centre ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$) interstitial sites by lithium ions. Evidence for a diffuse transition also arises from a change in slope of the ionic conductivity plot near 800 K and substantial shifts in the T_{2g} Raman mode above this temperature (Carron 1990).

In the present work we report the first Brillouin scattering measurements on Li_2S : these high temperature studies can be directly compared with results of the other experimental approaches discussed above and with the well-documented studies on the halide fluorites.

Brillouin spectra were excited using the 488 nm line from an argon-ion laser and analysed with a triple-pass Fabry–Perot interferometer as discussed previously in some

Table 1. Velocities of longitudinal (V_L) and transverse (V_T) acoustic phonon modes in a cubic crystal for [100] and [110] propagation directions.

	[100]	[110]
V_L	$(C_{11}/\rho)^{1/2}$	$[(C_{11} + C_{12} + 2C_{44})/2\rho]^{1/2}$
$V_T(1)$	$(C_{44}/\rho)^{1/2}$	$(C_{44}/\rho)^{1/2}$
$V_T(2)$	$(C_{44}/\rho)^{1/2}$	$[(C_{11} - C_{12})/2\rho]^{1/2}$

detail (Ngoepe and Comins 1987, Comins *et al* 1990). The acoustic mode frequencies and equivalent Brillouin frequency shifts are given by

$$\Delta\omega_B = (2nV\omega_0/c) \sin(\theta/2) \quad (1)$$

where V is the velocity of the acoustic phonons causing the scattering, n is the refractive index of the crystal, ω_0 is the frequency of the incident light and θ is the scattering angle, chosen as 90° .

The phonon propagation directions namely [100] and [110] were chosen such that the modes were purely longitudinal (L) or transverse (T) in character and their velocities bear the simplest relationship to the elastic constants C_{ij} . Table 1 gives the mode character and the respective elastic constant combinations. From equation (1) it follows that $(\Delta\omega_B)^2$ is proportional to the appropriate elastic constant or combination thereof, provided the ratio n^2/ρ is slowly varying (Comins *et al* 1990).

Two crystals of Li_2S were cut and polished to permit a study of phonon propagation along the directions given in table 1. The crystals required special care in their preparation as they are extremely hygroscopic. Accordingly x-ray orientation and sawing procedures were carried out with the crystal surfaces protected by medicinal paraffin. Polishing of the oriented cubes of approximate dimensions $3 \times 3 \times 3 \text{ mm}^3$ was carried out within a dry-bag fed by high-purity, dried nitrogen gas. Dry-polishing using $5 \mu\text{m}$ alumina powder provided adequate crystal surfaces; these were not as good as those normally obtained using fluid-based polishing media, but the latter could not be used owing to immediate attack on the crystal surfaces. The polished crystals were then encapsulated under high-purity argon gas in silica capsules. A matched recess cut in the base of the capsule preserved the crystal orientation. They were then mounted in an optical furnace and accurately aligned with respect to the incoming laser beam. In our usual procedure, crystal orientations are checked subsequent to polishing and if necessary, corrections are made. In the present case of a hygroscopic crystal this was not possible, and orientations were checked subsequent to the experimental runs at high temperature. Appropriate corrections to the mode velocities for crystal misorientation were calculated using the procedures of Every (1980). These proved negligibly small.

In figure 1 we show results for the [100] phonon propagation direction: $(\Delta\omega_B)^2$ corresponding to the longitudinal (L) and transverse (T) acoustic modes related to the elastic constants C_{11} and C_{44} , respectively, are plotted as a function of temperature. Corresponding results for the [110] phonon propagation direction are shown in figure 2. Here the variation of $(\Delta\omega_B)^2$ for the transverse (T) mode corresponding to the elastic constant combination $\frac{1}{2}(C_{11} - C_{12})$ is shown, together with the behaviour of C_{12} calculated using values from the measured modes. For some modes the Brillouin scattered light intensity was too weak to be detected near ambient temperature, but increased

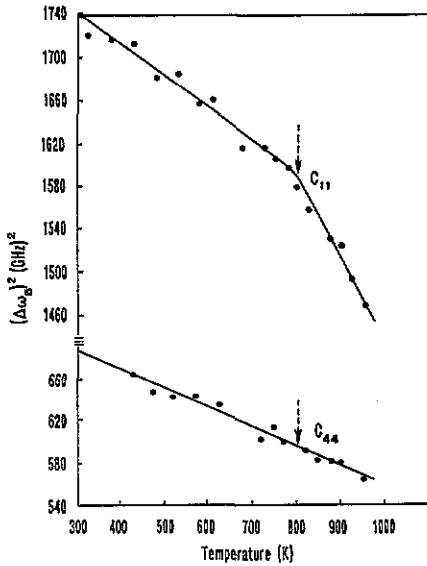


Figure 1. The temperature variation of the square of the Brillouin frequency shifts $(\Delta\omega_B)^2$ for the acoustic modes in the $[100]$ phonon propagation direction. The modes are indicated by their associated elastic constants C_{11} and C_{44} , respectively.

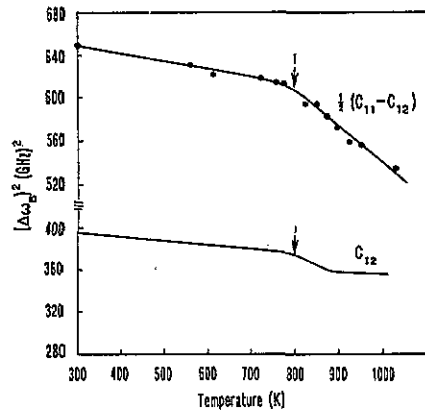


Figure 2. The temperature variation of $(\Delta\omega_B)^2$ for the transverse acoustic mode in the $[110]$ direction corresponding to elastic constant combination $\frac{1}{2}(C_{11} - C_{12})$. The variation with temperature of C_{12} is also shown, as calculated from the measured data.

sufficiently at higher temperatures as expected from the relation between the Rayleigh ratio and temperature (Cummins and Schoen 1972).

The behaviour of the mode frequencies and their associated elastic constants closely follows the pattern established for the pure fluorites undergoing a diffuse transition to the superionic state (Comins *et al* 1990). There is an initial linear decrease with temperature associated with thermal expansion and this is accounted for by the quasi-harmonic theory of Garber and Granato (1975). Above 800 K there are substantial decreases in C_{11} , $\frac{1}{2}(C_{11} - C_{12})$ and C_{12} whereas C_{44} is essentially unaffected.

Accordingly the results can be interpreted in terms of the current model of the diffuse transition: here attractive interactions between defects result in a reduction in the effective defect formation energy and lead to a co-operative transition in which a sublattice becomes partially disordered (Catlow *et al* 1978, Chadwick 1983). In the case of fluorites, the evidence strongly supports anion Frenkel disorder. In the present case of the anti-fluorite compound Li_2S , the behaviour of the elastic constants suggests lithium Frenkel disorder. This interpretation is in agreement with that of Buehrer *et al* (1991) in their evaluation of their neutron scattering results. Further work will include computational simulations of the disorder in a manner similar to studies on the fluorites (Catlow *et al* 1978) and LaF_3 (Ngoepe *et al* 1990).

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